The State of New Hampshire
Department of Environmental Services

Thomas S. Burack, Commissioner

MEMORANDUM

To: Ted Diers, NHDES
Dean Peschel, Great Bay Municipal Coalition
Steve Jones, UNH
Tom Gregory, UNH

From: Matthew A. Wood, NHDES

Date: April 13, 2016; Amended July 28, 2016

Re: Quality Assurance of 2015 Dover Wastewater Treatment Facility Assessment Study & Cocheco River Sonde Deployment report, submitted by Dr. Stephen H. Jones, Thomas K. Gregory, Thomas Langley & Alexi Bunda, University of New Hampshire, Jackson Estuarine Laboratory

PURPOSE

The purpose of this memorandum is to document the results of quality assurance checks on the 2015 water quality data collected by the University of New Hampshire – Jackson Estuarine Laboratory (UNH) for the Dover Wastewater Treatment Facility Assessment Study & Cocheco River Sonde Deployment Study. NHDES reviewed these data to ensure that they are of sufficient quality to be used in management decisions and for Section 305b water quality assessments.

OVERVIEW

The Dover Wastewater Treatment Facility Assessment Study & Cocheco River Sonde Deployment Study was conducted by the University of New Hampshire Jackson Estuarine Laboratory in 2015 under contract from the Great Bay Municipal Coalition. The final datasets for the study were delivered to NHDES on January 14, 2016 and February 18, 2016. NHDES conducted a preliminary review of the datasets and concluded that there were a number of quality assurance-related questions that needed to be addressed. One of the primary issues with the datasets was that the locations of the datasondes and grab samples were not clear. Ultimately, the major inconsistencies were resolved through an email exchange between NHDES and University of New Hampshire Jackson Estuarine Laboratory dated February 10, 2016. As a result, a new unique station ID was created (UPR6A) because it was discovered that the location that was sampled was not the same as initially indicated in the QAPP.

Once the additional information was received, NHDES began quality assurance checks to uncover potential errors. Some information was still missing from the datasets and NHDES made every effort to resolve these remaining issues directly with monitoring staff at UNH so that the dataset could be finalized. A small fraction of the results did not meet acceptance criteria and

were marked with an "N" in the ResultsValid field. All quality control steps and changes to the datasets have been documented in this memo.

A project has been created in the NHDES Environmental Monitoring Database (EMD) to house the data from this study with a project identifier of "JEL-GBMC-2015". The project ID represents the organization that collected the samples (Jackson Estuary Laboratory - JEL), followed by the organization that commissioned the study (Great Bay Municipal Coalition-GBMC), followed by the year in which the study was conducted (2015).

STATION NAMING CONVENTION

Where applicable, site identifications were renamed to conform to the unique identification requirements of the NHDES Environmental Monitoring Database. GPS coordinates collected in the field were used to create station locations. All Stations were assigned to Project ID "JEL-GBMC-2015" in the EMD.

Final EMD Station Designation	Final EMD Station Coordinates Created By	Surface Water Sampling Location from the Study Report	Datasonde Sampling Location
UPR6A	GPS Coordinates	GBMC15-01& 0057	Upper Piscataqua River
UPR4	Existing EMD Station (GPS Coordinates)	GBMC15-02 & UPR4	Upper Piscataqua River
CR7	Existing EMD Station (GPS Coordinates)	GBMC15-03 & CR7	Cocheco River Estuary

DATA CENSORING

If a result was less than the Reportable Detection Limit (RDL), it was flagged with a "<" in the qualifier field and the reported result was replaced by the RDL value. The highest censoring rates were for ammonia (43.1%) and nitrite + nitrate (15.3%). The RDL and percent of data that were censored are shown in the following table. Overall, 4.4% of the results that had RDLs that were censored.

Parameter	Reported Value Range	RDL	Units	Censored Samples	Total Samples	Percent Censored
NITROGEN, AMMONIA AS N	-4.4 - 5.7	6.3	UG/L	31	72	43.1%
NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	0 - 0.003	0.004	MG/L	11	72	15.3%
NITROGEN, ORGANIC	0.03	0.05	MG/L	1	72	1.4%
SILICA AS SIO2	0.01	0.04	MG/L	1	72	1.4%
Grand Total (all parameters with a RDL)				44	1006	4.4%

OUTLIER CHECK

NHDES checked the 2015 grab sample dataset for outliers by comparing the summary statistics from 2015 against the summary statistics from the GBNERR program from 1988-2014, which

analyzes many of the same parameters. This check did not identify any anomalous results. The range of results from the 2015 dataset is shown in the following table.

Parameter	N	Min.	Ave.	Max.	Units
CARBON, DISSOLVED ORGANIC	72	1.54	2.29	4.61	MG/L
CARBON, TOTAL SUSPENDED	72	293.4	742.2	3,139.8	UG/L
CHLOROPHYLL A, CORRECTED FOR PHEOPHYTIN	71	1.9	6.1	28.8	UG/L
DISSOLVED OXYGEN	122	6.1	8.3	12.8	MG/L
DISSOLVED OXYGEN SATURATION	122	10.8	108.4	175.9	%
LIGHT ATTENUATION COEFFICIENT	37	0.7	1.0	2.2	1/M
TOTAL NITROGEN	72	0.2	0.3	0.8	MG/L
NITROGEN, AMMONIA AS N	72	< 6.3	13.7	51.7	UG/L
NITROGEN, TOTAL DISSOLVED	72	0.114	0.193	0.316	MG/L
NITROGEN, NITRITE (NO2) + NITRATE (NO3) AS N	72	< 0.004	0.025	0.073	MG/L
NITROGEN, DISSOLVED ORGANIC	72	< 0.050	0.157	0.311	MG/L
NITROGEN, SUSPENDED	72	29.0	90.2	396.4	UG/L
PH	117	7.5	7.9	10.8	NONE
PHEOPHYTIN-A	71	0.5	1.4	4.1	UG/L
PHOSPHORUS	72	21.0	60.1	139.0	UG/L
PHOSPHORUS, ORTHOPHOSPHATE AS P	72	18.6	27.0	42.5	UG/L
SALINITY	122	5.7	26.5	30.6	PSS
SILICA AS SIO2	72	< 0.040	0.708	2.327	MG/L
SOLIDS, TOTAL SUSPENDED	72	6.4	22.1	37.9	MG/L
TEMPERATURE WATER	122	4.4	21.2	26.5	DEG C
TURBIDITY	117	0.9	3.0	14.5	NTU

FIELD REPLICATE COMPARISON

In 2015, no laboratory or field duplicates were collected associated with the Dover Wastewater Treatment Facility Assessment Study & Cocheco River Sonde Deployment sampling efforts by Dr. Jones and Mr. Gregory (UNH). Section 7 of the QAPP (Dover Wastewater Treatment Facility Assessment Study & Cocheco River Sonde Deployment QAPP) dated December 15, 2015, outlines performance criteria for comparing the precision of laboratory and field duplicates, however, the QAPP fails to outline the number of field duplicates planned, a 10 percent minimum is the target set in the other QAPPs and field sampling efforts by Dr. Jones and Mr. Gregory. Because no duplicates were collected this performance measure cannot be directly evaluated for this project. NHDES understands the sampling staff, training protocol, sampling methods, and sampled parameters to be consistent between this and the other projects (namely the NERRs SWMP, the 2011 Squamscott River Dissolved Oxygen Study Field Sampling & Monitoring, and the Cocheco River, Salmon Falls River, & Upper Piscataqua River Sediment-Oxygen Demand & Rate of Metabolism Study Field Sampling & Monitoring) administered by Dr. Jones and Mr. Gregory on the Great Bay Estuary.

Section 3.1.10 Data Quality, of the 2014 Section 305(b) and 303(d) Consolidated Assessment and Listing Methodology (CALM; available at: http://des.nh.gov/organization/divisions/water/wmb/swqa/2014/documents/2014-calm.pdf), states that for data to be used to make final assessment decisions it must be defensible with

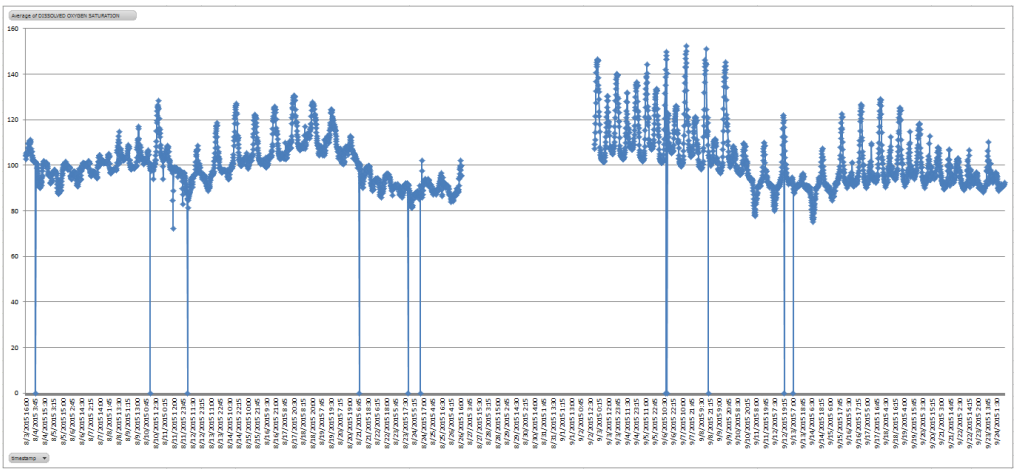
adequate sampling staff, training protocol, sampling methods, and QA duplicates. If this were a solitary project it would be DES' judgment that although a QA/QC plan is available, protocols were not robust as no field duplicate samples were collected or analyzed. Because of this factor, DES' confidence in this data would fall into the "Low" category as indicated in Table 3-8 of the 2014 CALM. As such, all data associated to project code JEL-GBMC-2015 would not be used to make full assessment decisions and instead would only be utilized to make screening level assessments.

However, the sampling effort in question by Dr. Jones and Mr. Gregory is not their solitary project. NHDES would like to confirm with the researchers that the sampling staff, training protocol, sampling methods, and QA duplicates are consistent between this and the other projects administered by Dr. Jones and Mr. Gregory on the Great Bay Estuary. Further, NHDES would like to confirm that in their totality, those projects administered by Dr. Jones and Mr. Gregory on the Great Bay Estuary meet the 10 percent minimum field duplicate target in the 2015 field season. If those two elements could be confirmed, NHDES' confidence in the integrity of the dataset would be high.

ANOMALOUS DATASONDE READINGS DURING DEPLOYMENT

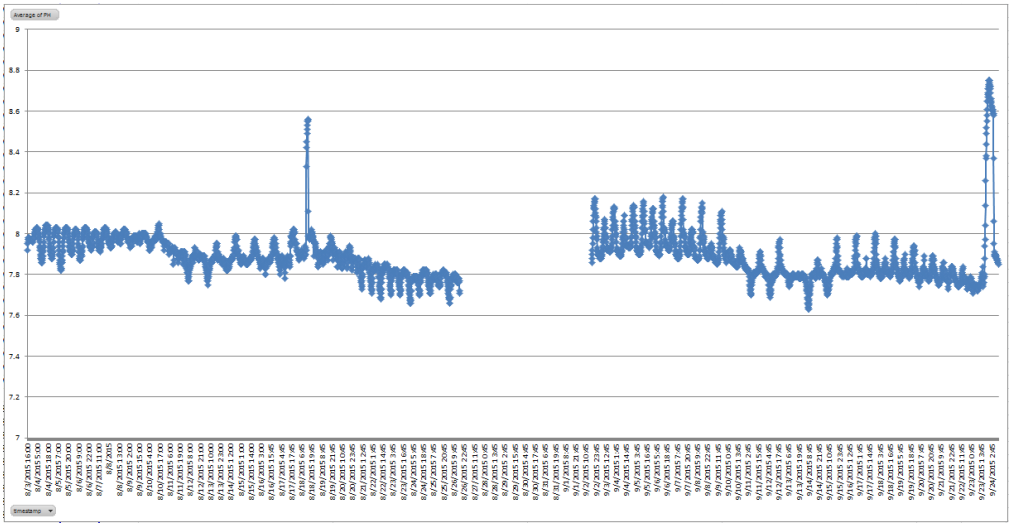
The UNH laboratory conducted a preliminary review of the datasonde data and flagged values that they thought were atypical. However, no determination was made as to whether the data should be considered valid or whether it should be invalidated. Therefore, all datasonde deployments were reviewed by NHDES for anomalous readings, sensor drift, and changes in readings before and after sonde replacement. All anomalous readings identified by NHDES and the determinations made are below:

UPR6A:
Anomalously low dissolved oxygen data was identified on 11 separate occasions. They occurred on 08/04/2015 at 04:30:00 EDT, 08/10/2015 at 06:00:00 EDT, 08/12/2015 at 05:30:00 EDT, 08/21/2015 at 07:30:00 EDT, 08/23/2015 at 21:45:00 EDT, 08/24/2015 at 13:15:00 EDT, 09/06/2015 at 13:15:00 EDT, 09/06/2015 at 14:45:00 EDT, 09/08/2015 at 19:15:00 EDT, 09/12/2015 at 19:30:00 EDT, and 09/13/2015 at 07:15:00 EDT (dissolved oxygen % sat. = 0.0 and dissolved oxygen mg/L = 0.0). The readings taken two hours prior to and two hours following these measurements averaged 101.2% and 7.63 mg/L, therefore the anomalously low dissolved oxygen measurements were invalidated.



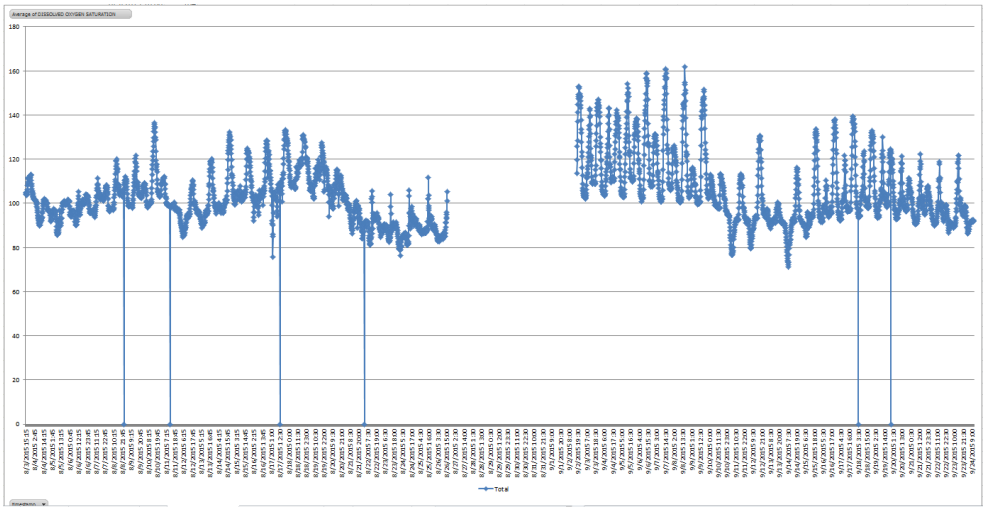
Aberrant pH data was identified starting on 09/18/2015 at 19:00:00 EDT through 15:30:00 EDT (average of 8.5). The readings taken two hours prior to and two hours following these measurements averaged 7.9, therefore the anomalous pH measurements on 08/18/2015 from 13:00:00 EDT through 15:30:00 EDT were invalidated.

Aberrant pH data was also identified starting on 08/23/2015 at 13:00:00 EDT through 09/24/2015 at 05:30:00 EDT (average of 8.6). Investigation into this aberrant data led to the realization that the datasonde was potentially recovered and removed from the water on 09/23/2015 at 17:47 EDT (Table 4 in the Filed Sampling & Monitoring Report). NHDES requested confirmation of the sonde removal date from the project manager and QA officer on 03/17/2016. Upon the issuance of this memo no response had been received. Considering the uncertainty of the sonde removal date and the aberrant pH data seen in the data record, NHDES chose to invalidate all data for all parameters beginning on 9/23/2016 at 18:00:00 EDT through the end of the data record on 9/24/2015 at 11:30:00 EDT (71 measurements).

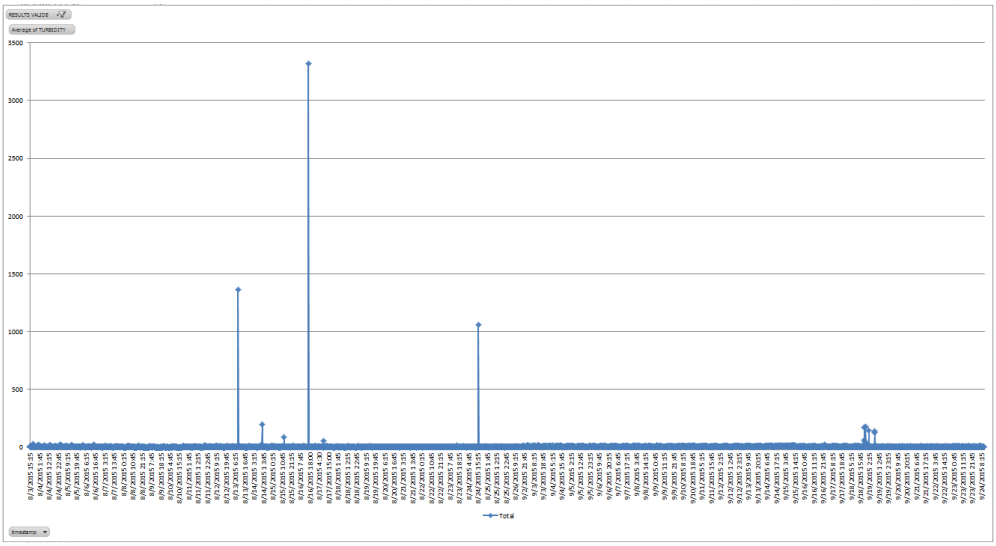


UPR4:

Anomalously low dissolved oxygen data was identified on six separate occasions. They occurred on 08/09/2015 at 00:15:00 EDT, 08/11/2015 at 12:45:00 EDT, 08/17/2015 at 12:45:00 EDT, 08/22/2015 at 03:30:00 EDT, 09/18/2015 at 04:00:00 EDT, and 09/19/2015 at 22:45:00 EDT (dissolved oxygen % sat. = 0.0 and dissolved oxygen mg/L = 0.0). The readings taken two hours prior to and two hours following these measurements averaged 103.5% and 7.28 mg/L, therefore the anomalously low dissolved oxygen measurements were invalidated.

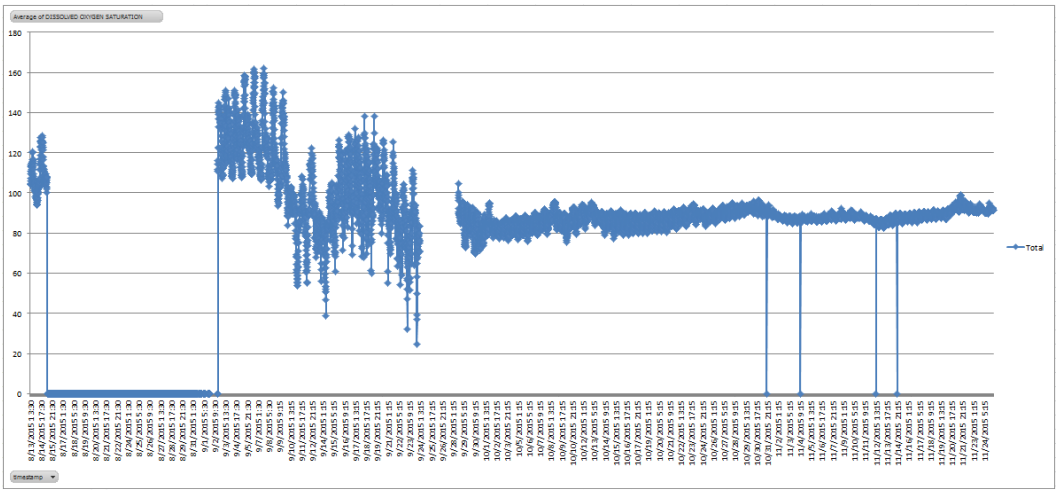


Aberrant turbidity data was identified on 08/13/2015 at 09:45:00 EDT, 08/16/2015 at 16:45:00 EDT and 08/24/2015 at 16:15:00 EDT (1,366, 3,320, and 1,062 NTUs, respectively). The readings taken two hours prior to and two hours following these measurements averaged 3.8 NTUs, therefore the anomalously high turbidity measurements were invalidated.

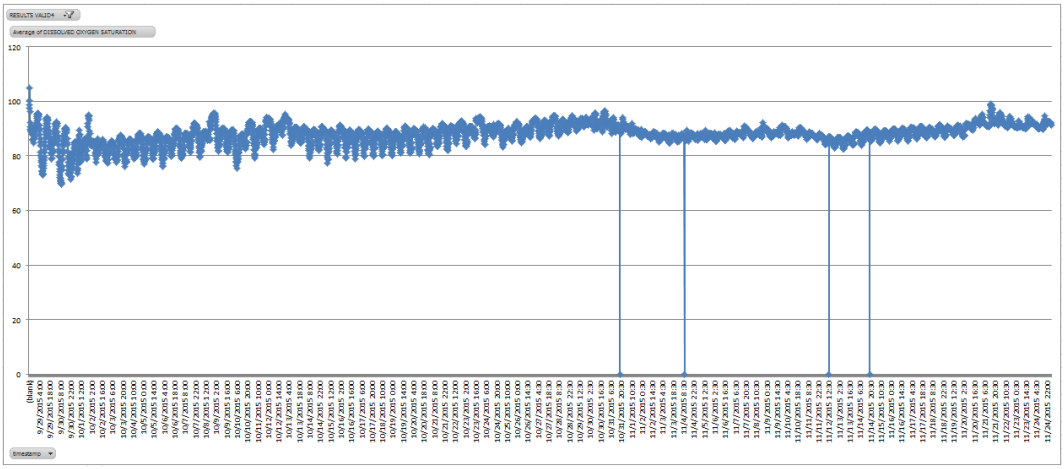


CR7:

The narrative contained within the Filed Sampling & Monitoring Report describing the datasonde deployments indicates that the two datasondes (Manta2 & YSI 6600) deployed at station CR7 experienced technical problems. The data from the Manta2 was unrecoverable and the aberrant data form the YSI 6600 was first apparent in the dissolved oxygen data, which culminated in the complete failure of the datasonde. Because the sondes were malfunctioning and eventually failed completely, NHDES has chosen to invalidate all data for all parameters collected with the YSI 6600 datasonde during the deployment beginning on 08/13/2015 at 13:30:00 EDT and ending on 09/03/2015 at 10:30:00 EDT (the original memo dated 04/13/2016 mistakenly specified the data collected with a Manta2 datasonde deployed between 09/02/2015 at 17:30:00 EDT and 09/24/2015 at 11:15:00 EDT as invalid).



Anomalously low dissolved oxygen data was identified on four separate occasions. They occurred on 10/31/2015 at 19:00:00 EDT, 11/04/2015 at 10:00:00 EST, 11/12/2015 at 12:45:00 EST, and 11/14/2015 at 19:30:00 EST (dissolved oxygen % sat. = 0.0 and dissolved oxygen mg/L = 0.0). The readings taken two hours prior to and two hours following these measurements averaged 87.6% and 8.69 mg/L, therefore the anomalously low dissolved oxygen measurements were invalidated.



OTHER ISSUES

Prior to review of the data, NHDES invalidated all chlorophyll measurements for stations CR7 UPR4 and UPR6A, and inserted comments indicating that they are to be considered as estimated data. Turner Designs, which is the manufacture of the chlorophyll probe used on the Eureka sondes, stipulates that "*in vivo* chlorophyll analysis is the measurement of chlorophyll fluorescence within a living cell. However, without comparisons to extractive analysis, *in vivo* readings are qualitative in nature". The comparison of the *in vivo* datasonde readings to those that underwent the extractive analysis conducted by UNH showed a poor correlation between the *in vivo* and wet chemistry results for stations CR7 and UPR6A.

Unlike stations CR7 and UPR6A, the December 31, 2015 Field Sampling & Monitoring Report shows a high correlation (Pearson correlation coefficient (r^2) of 0.918) between the sonde data and the wet chemistry results taken 0.5m above the sediment for station UPR4. The report further states that this relationship "suggests that the two approaches for determining chlorophyll *a* concentrations are related and valid." Although NHDES does not disagree that there is a relationship between the two measures, the data needs to be further examined to determine if a significant relationship exists, as the report stops short of making a recommendation on how to use or interpret the data. It should also be noted that the *in vivo* datasonde readings are a measure of total chlorophyll, while the samples that underwent extractive analysis are a measure of chlorophyll *a* corrected for pheophytin.

NHDES encourages to the Municipal Coalition to continue developing a relationship between the sonde data and the wet chemistry results. However, at this time all chlorophyll data collected by the Eureka sondes for the entire deployments at stations CR7, UPR4 and UPR6A have been invalidated. NHDES suggests that when conducting future comparisons of the two techniques that only discrete values be compared to make the analysis more robust. Specific to this analysis, the datasondes were deployed approximately 0.5m above the sediment, therefore only the grab samples that were collected at the same relative depth should be compared. Furthermore, the subject report states that "wet chemistry samples were compared to sonde data based on average of 3 readings before and after the time for grab sample collection at each site." Because of the variability in chlorophyll data it is inappropriate to use average readings taken over a 1.5 hour period for comparison to a sample collected at an explicit time. Only the datasonde reading taken closest to the time of the grab sample should be compared.